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Analysis of  $S=5/2$  Ions in  $C_2$  Symmetry.  
Application to  $Fe^{3+}$  in Quartz.**



**U.S. DEPARTMENT OF COMMERCE  
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# TECHNICAL NOTE 372

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MATHEMATICAL TECHNIQUES FOR EPR  
ANALYSIS OF  $S = 5/2$  IONS IN  $C_2$  SYMMETRY.  
APPLICATION TO  $Fe^{3+}$  IN QUARTZ.

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Mathematical Techniques for EPR Analysis of  $S = 5/2$  Ions  
in  $C_2$  Symmetry. Application to  $Fe^{3+}$  in Quartz

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ABSTRACT

Various formulas and mathematical techniques useful for the analyses of the EPR spectra of ions of angular momentum  $5/2$  in sites of  $C_2$  symmetry are presented. Special emphasis is given to the spectrum of  $Fe^{3+}$  in synthetic brown quartz. Included are: matrix elements of the Racah operators for arbitrary direction of the axis of quantization relative to the crystalline electric field axes, spectral line-position formulas based upon a usage of second-order perturbation theory which is somewhat different from the usual, and line-intensity formulas.

Key Words: electron paramagnetic resonance; ferric ion; synthetic quartz

The purpose of this paper is to present various mathematical formulas and techniques which are useful for the analysis of the EPR spectra of  $S = 5/2$  ions in fields of  $C_2$  symmetry. Special application is made to the spectrum of  $Fe^{3+}$  in synthetic brown quartz.<sup>1,2</sup>

$Fe^{3+}$  is an S-state ion with spin  $S = 5/2$ . In quartz it apparently finds itself in a crystalline electric field environment of two-fold symmetry,  $C_2$ .<sup>1</sup> The crystalline potential may be developed in spherical harmonics  $Y_{\ell m}$ . Only  $\ell = 2$  and  $4$  terms need be considered since the matrix elements of  $Y_{\ell m}$  for other  $\ell$  values vanish.<sup>3,4</sup> The  $C_2$  symmetry eliminates odd  $m$  values. Since the crystal field potential must be real, it finally can be written as

$$V_{20} + V_{22} + V_{40} + V_{42} + V_{44}, \quad (1)$$

where

$$V_{\ell m} \equiv a_{\ell m} Y_{\ell m} + a_{\ell m}^* Y_{\ell, -m}. \quad (2)$$

We have here used spherical harmonics with the property

$$Y_{\ell, -m} = (-1)^m Y_{\ell m}^*. \quad (3)$$

In constructing the Hamiltonian it is convenient and conventional to use spin operators which have the same transformation properties as the  $Y_{\ell m}$ . Bleaney and Stevens<sup>3</sup> have discussed one such scheme, which has been reviewed by Hutchings.<sup>4</sup> Kikuchi and Matarrese<sup>5</sup> have used a more systematic prescription, based upon the Racah operators,<sup>6</sup>  $T_m^{(\ell)}$ . These were used in the analysis of  $Fe^{3+}$  in quartz,<sup>1</sup> and will be used here. The  $T_m^{(\ell)}$  are generated by the process

$$T_{m-1}^{(\ell)} = [\ell(\ell+1) - m(m-1)]^{-\frac{1}{2}} [S_-, T_m^{(\ell)}]. \quad (4)$$

With the normalization of Kikuchi and Matarrese,<sup>5</sup> the  $T_m^{(\ell)}$  necessary for the present purposes are

$$\begin{aligned} T_0^{(2)} &= S_r^2 - X/3, \\ T_{\pm 2}^{(2)} &= S_{\pm}^2 / \sqrt{6}, \\ T_0^{(4)} &= [35S_r^4 - 30XS_r^2 + 25S_r^2 - 6X + 3X^2] \\ T_{\pm 2}^{(4)} &= -S_{\pm}^2 [X - 9 \mp 14S_r - 7S_r^2] \sqrt{10}/8, \\ T_{\pm 4}^{(4)} &= S_{\pm}^4 \sqrt{70}/16, \end{aligned} \quad (5)$$



where

$$X \equiv S(S+1) . \quad (6)$$

In Eqs. (5), the subscript r refers to the two-fold axis of the crystalline electric field. The remaining two orthogonal axes will be denoted by p and q. The raising and lowering operators,  $S'_{\pm}$ , of Eqs. (5) are defined by

$$S'_{\pm} = S_p \pm i S_q . \quad (7)$$

The complete spin Hamiltonian for an S-state ion (excluding nuclear spin interactions) in an environment of  $C_2$  symmetry, and an external magnetic field  $\underline{H}$  in an arbitrary direction, is

$$\begin{aligned} \mathcal{H} = & \beta_o \underline{H} \cdot \underline{\tilde{g}} \cdot \underline{S} + C_{20} T_0^{(2)} + C_{22} (T_2^{(2)} e^{-2i\lambda_{22}} + T_{-2}^{(2)} e^{2i\lambda_{22}}) + C_{40} T_0^{(4)} \\ & + C_{42} (T_2^{(4)} e^{-2i\lambda_{42}} + T_{-2}^{(4)} e^{2i\lambda_{42}}) + C_{44} (T_4^{(4)} e^{-4i\lambda_{44}} + T_{-4}^{(4)} e^{4i\lambda_{44}}). \end{aligned} \quad (8)$$

Here  $\beta_o$  is the Bohr magneton (used here as positive) and  $\tilde{g}$  is the g-tensor. The coefficients of the  $T_m^{(\ell)}$  have been written as a real number,  $C_{\ell m}$ , multiplying a phase factor. The  $C_{\ell m}$  clearly can be taken as positive without loss of generality, for  $|m| > 0$ . The  $C_{20}$  and  $C_{40}$  must be real but may be positive or negative.

To use perturbation theory at high fields, one diagonalizes the Zeeman term. If the g-tensor is isotropic, as is the usual case for S-state ions, and has been shown to be true for iron-doped quartz,<sup>1</sup> the axis of quantization is just the direction of  $\underline{H}$ . Let this axis be the z-axis of any x, y, z orthogonal coordinate system. The direction of the z-axis relative to the p, q, r crystalline electric field axes is given by the Euler angles  $\alpha$ ,  $\beta$ , in the convention of Rose.<sup>7</sup> The axes and angles are

illustrated in Figure 1.

The transformation equations from the  $S_r$ ,  $S'_\pm$  operators to the  $S_z$ ,  $S_\pm$  operators are

$$S'_\pm = \frac{1}{2} e^{\pm i\alpha} [S_\pm (\cos \beta + 1) + S_\mp (\cos \beta - 1)] + S_z e^{\pm i\alpha} \sin \beta, \quad (9)$$

$$S_r = -(S_+ + S_-) \frac{1}{2} \sin \beta + S_z \cos \beta,$$

where

$$S_\pm = S_x \pm iS_y. \quad (10)$$

The matrix elements of the  $T_m^{(\ell)}$  in the representation of the eigenstates  $|M\rangle$ ,  $-S \leq M \leq S$ , of  $S_z$ , are given in Tables I - V. Table VI lists, for the reader's convenience, the associated Legendre polynomials  $P_{\ell m}$  for  $0 \leq \ell \leq 4$  and  $m \leq \ell$ , which occur in Tables I and III. The diagonal elements of the Zeeman term are of course just  $g\beta_o HM$ .

For reasons which will be discussed, we have used a perturbation analysis somewhat different from the usual one.<sup>8</sup> In the conventional perturbation theory, one develops the eigenstates and eigenvalues in perturbation series as

$$|E_M\rangle = |M\rangle + |M^{(1)}\rangle + |M^{(2)}\rangle + \dots, \quad (11)$$

$$E_M = E_M^{(0)} + E_M^{(1)} + E_M^{(2)} + \dots, \quad (12)$$

where

$$\mathcal{H} = \mathcal{H}_0 + V, \quad (13)$$

$$\mathcal{H}_0 |M\rangle = E_M^{(0)} |M\rangle, \quad (14)$$

$$\mathcal{H} |E_M\rangle = E_M |E_M\rangle, \quad (15)$$



and  $V$  is the perturbation. Substituting Eqs. (11) - (14) into (15), and performing the standard manipulations,<sup>9</sup> one obtains in the nondegenerate case,

$$E_M^{(1)} = \langle M | V | M \rangle, \quad (16)$$

$$E_M^{(2)} = \sum_{M'}^{(M)} \frac{|\langle M | V | M' \rangle|^2}{E_M^{(0)} - E_{M'}^{(0)}}, \quad (17)$$

$$E_M^{(3)} = \sum_{M'}^{(M)} \sum_{M''}^{(M)} \frac{\langle M | V | M' \rangle \langle M' | V | M'' \rangle \langle M'' | V | M \rangle}{(E_M^{(0)} - E_{M'}^{(0)}) (E_M^{(0)} - E_{M''}^{(0)})} \quad (18)$$

$$- \sum_{M'}^{(M)} \frac{|\langle M | V | M' \rangle|^2 \langle M | V | M \rangle}{(E_M^{(0)} - E_{M'}^{(0)})^2}.$$

The notation  $\sum_{M'}^{(M)}$ , for example, means that  $M' = M$  is excluded from the summation on  $M'$ . Now for  $\text{Fe}^{3+}$  in quartz, it turns out that  $C_{20}$  is numerically quite large: its correction to the line-position values is sometimes more than 30% of the free-ion value. Thus  $\langle M | V | M \rangle$  is "large." It does not occur in the second-order term  $E_M^{(2)}$ , but does occur in the third order terms, with the result that for certain lines and certain orientations, the third-order terms should not be neglected. However, for  $\beta = 0^\circ$  (H parallel to the two-fold axis), the  $T_0^{(2)}$  term lies completely on the diagonal. Therefore by including it in  $\mathcal{H}_0$ , a vast improvement in accuracy in the second-order calculations is achieved. We systematically have put all diagonal elements of  $V$  in with  $\mathcal{H}_0$ . This renormalizes  $E_M^{(0)}$ , and gives the following perturbation corrections:

$$E_M^{(1)} = 0, \quad (19)$$

$$E_M^{(2)} = \sum_{M'}^{(M)} \frac{|\langle M|V|M'\rangle|^2}{E_M^{(0)} - E_{M'}^{(0)}} \quad (20)$$

$$E_M^{(3)} = \sum_{M'}^{(M)} \sum_{M''}^{(M)} \frac{\langle M|V|M'\rangle \langle M'|V|M''\rangle \langle M''|V|M\rangle}{(E_M^{(0)} - E_{M'}^{(0)}) (E_M^{(0)} - E_{M''}^{(0)})} \quad (21)$$

At  $\beta = 0^\circ$  the third-order terms in this reformulation are entirely negligible at K-band frequencies in iron-doped quartz. For  $\beta = 90^\circ$ , the  $T_0^{(2)}$  term has off-diagonal elements, and the two perturbation treatments tend to be equivalent in their results. (These conclusions could be drawn as soon as rough estimates of the  $C_{\ell m}$  were known).

The line-position formulas, through second order in the modified perturbation treatment, are given in Table VII. The definitions of the terms appearing in this Table are given in Table VIII.  $H_1$  corresponds to the  $(E_{5/2} - E_{3/2})$  transition,  $H_2$  to the  $(E_{3/2} - E_{1/2})$  transition and so on.

One other point may be discussed here.  $C_2$  symmetry, by itself, does not define the orientations of the p and q crystalline field axes. For example, from a crystallographic analysis, one knows that the optic axis of quartz (Z) lies in the p, q plane, and that the X-axis of the quartz coincides with the two-fold axis of one of the sites at which the  $Fe^{3+}$  resides. (See Fig. 1). The angle  $\alpha$ , defined as measured from the p-axis, is not immediately measurable. The measured angle is  $\alpha - \Theta$ , where  $\Theta$  is the (arbitrary) angle from p to Z. For example, when  $\underline{H}$  is parallel to the optic axis, parameters such as  $C_{22} \cos 2(\Theta - \lambda_{22})$  and  $C_{44} \sin 4(\Theta - \lambda_{44})$  appear in the line position formulas. Thus the angles  $\lambda_{22}$  and  $\lambda_{44}$ , which locate the  $V_{22}$  and  $V_{44}$  lobes in the p, q plane, can be measured only relative to  $\Theta$ , that is, relative to the optic

axis. In reference 1, we arbitrarily set  $p$  to coincide with  $Z$  (i. e.,  $\Theta = 0$ ); this was purely for convenience.

We turn finally to the line-intensity formulas. We consider only the case for which  $\underline{H}$  is along the  $r$ -axis, and the microwave field  $H_1$  lies in the  $p, q$  plane (Fig. 2). It was for this situation that an interesting effect was uncovered in iron-doped quartz: for  $H_1$  nearly perpendicular to the optic axis, and for small values of  $H$ , several lines are readily observable. However, when  $\underline{H}_1$  is rotated into orientations near the  $Z$ -axis, all the lines disappear into the noise. Substitution of the parameter values, determined from the high-field data, into the line-intensity formulas shows that this effect is to be expected, and further confirms our choice of parameter values,<sup>1</sup> including the orientations of the crystalline field lobes. However, line intensities are difficult to measure accurately, and so the determination of the parameters from line-position analyses is still to be preferred.

The interaction between the ion and the microwave field is (see Fig. 2)

$$\begin{aligned} \mathcal{H}_1 &= \frac{1}{2} g \beta_o H_1 \left[ S_p \cos \Phi + S_q \sin \Phi \right] \\ &= \frac{1}{2} g \beta_o H_1 \left[ S_+ e^{-i\Phi} + S_- e^{i\Phi} \right] \end{aligned} \quad (22)$$

Here we have used Eqs. (7) and (9), setting both  $\alpha$  and  $\beta$  equal to zero. (The value of  $\alpha$  here is actually arbitrary, as it is in the spin-Hamiltonian matrix for  $\underline{H}$  parallel to the  $r$ -axis (Table IX). However, the same value of  $\alpha$  must be used in both places for consistency; we use  $\alpha = 0$ .)

For  $\underline{H}$  parallel to the  $r$ -axis, the  $6 \times 6$  matrix of the spin Hamiltonian separates into two independent  $3 \times 3$  matrices. This case

is given in Table IX. The  $|5/2\rangle$ ,  $|1/2\rangle$ , and  $|-3/2\rangle$  states couple together to form three exact eigenstates of the Hamiltonian, which we call  $|E_k^+\rangle$ ,  $k = 0, 1, 2$ . Similarly,  $|-5/2\rangle$ ,  $|-1/2\rangle$ , and  $|3/2\rangle$  couple to form  $|E_k^-\rangle$ . The secular equations for determining the energies  $E_k^\pm$  and eigenstates  $|E_k^\pm\rangle$  are thus cubic and can be solved analytically.

Writing

$$|E_k^\pm\rangle = a_k^\pm |\pm 5/2\rangle + b_k^\pm |\pm 1/2\rangle + c_k^\mp |\mp 3/2\rangle, \quad (23)$$

one finds the nonvanishing matrix elements of  $\mathcal{H}_1$  (Eq. (22)) in the  $|E_k^\pm\rangle$  basis to be

$$\begin{aligned} \langle E_\ell^- | \mathcal{H}_1 | E_k^+ \rangle = \frac{1}{2} g\beta_o H_1 \left\{ \sqrt{5} e^{i\Phi} (a_\ell^{-*} c_k^- + c_\ell^{+*} a_k^+) + 3e^{i\Phi} b_\ell^{-*} b_k^+ \right. \\ \left. + \sqrt{8} e^{-i\Phi} (b_\ell^{-*} c_k^- + c_\ell^{+*} b_k^+) \right\}. \end{aligned} \quad (24)$$

The line intensities are proportional to the absolute-value-squared of Eq. (24).

It is instructive first to consider two special cases. Assume that  $C_{42} = C_{22} = 0$  and that  $C_{44} \neq 0$ . From Table IX one sees at once that the states  $|\pm \frac{1}{2}\rangle$  are uncoupled from the remaining states, and hence are eigenstates of the spin Hamiltonian. Thus, for one value of  $k$  the coefficients  $b_k^\pm$  of Eq. (23) are unity, and  $a_k^\pm$  and  $c_k^\mp$  are zero, while for the other two values of  $k$ ,  $b_k^\pm$  is zero, and  $a_k^\pm$  and  $c_k^\mp$  are not. By inspection of Eq. (24), one sees that  $\langle E_\ell^- | \mathcal{H}_1 | E_k^+ \rangle$  then depends upon  $\Phi$  only through  $e^{i\Phi}$  or through  $e^{-i\Phi}$ , so that all line intensities are independent of  $\Phi$ . That is, although there are lobes of  $V_{44}$  in the  $p, q$  plane, the line intensities are uniform for  $\underline{H}_1$  anywhere in that plane.

Next consider  $C_{22} \neq 0$  and  $C_{44} = C_{42} = 0$ . This case is



more complicated than the preceding, but still quite tractable. By expressing both  $a_k^\pm$  and  $c_k^\mp$  in terms of  $b_k^\pm$  from the secular equations, one can draw the desired conclusion without further determining the coefficients or the energies. After a small amount of manipulation, one can write Eq. (24) as

$$\begin{aligned} \langle E_\ell^- | \mathcal{H}_1 | E_k^+ \rangle = g\beta_o H_1 b_\ell^{-*} b_k^+ & \left\{ 10 C_{22}^2 e^{i\Phi} \left( \frac{1}{(f_{-5}^- - E_\ell^-)(f_{-3}^- - E_k^+)} \right. \right. \\ & \left. \left. + \frac{1}{(f_3^- - E_\ell^-)(f_5^- - E_k^+)} \right) + \frac{3}{2} e^{i\Phi} \sqrt{6} C_{22} e^{-i(\Phi - 2\lambda_{22})} \left( \frac{1}{f_{-3}^- - E_k^+} + \frac{1}{f_3^- - E_\ell^-} \right) \right\}, \end{aligned} \quad (25)$$

where  $f_{-5}^- \equiv \langle -\frac{5}{2} | \mathcal{H} | -\frac{5}{2} \rangle$ ,  $f_3^- \equiv \langle \frac{3}{2} | \mathcal{H} | \frac{3}{2} \rangle$ , etc. Squaring the absolute value, one has

$$\begin{aligned} |\langle E_\ell^- | \mathcal{H}_1 | E_k^+ \rangle|^2 = (g\beta_o H_1)^2 |b_\ell^-|^2 |b_k^+|^2 & \left\{ (A_{k\ell} + B_{k\ell})^2 \cos^2 (\Phi - \lambda_{22}) \right. \\ & \left. + (A_{k\ell} - B_{k\ell})^2 \sin^2 (\Phi - \lambda_{22}) \right\}, \end{aligned} \quad (26)$$

where  $A_{k\ell}$  and  $B_{k\ell}$  are the coefficients of  $e^{i\Phi}$  and  $e^{-i(\Phi - 2\lambda_{22})}$ , respectively, within the braces of Eq. (25), and are real. In this case line-intensity extrema do exist, occurring at  $\Phi = \lambda_{22}$  and every  $90^\circ$  therefrom.

When  $C_{22}$ ,  $C_{42}$ , and  $C_{44}$  are all considered, the equations for the line-intensity extrema are quite complicated (transcendental) and we will not give them here. However, since  $C_{42}$ ,  $C_{44} \ll C_{22}$  for iron in quartz, we can expect that the line-intensity extrema will be shifted but slightly from the  $V_{22}$  lobes, and this is indeed the case

experimentally.<sup>1</sup> The coefficients  $a_k^\pm$ ,  $b_k^\pm$ ,  $c_k^\mp$  were determined by computer from the analytic solutions to the secular equations for many values of H, and the locations ( $\Phi$ ) of the maxima and minima in the line intensities were calculated. Agreement with these results is observed to within our ability to locate the intensity extrema experimentally.



M	5/2	3/2	1/2	- 1/2	- 3/2	- 5/2
5/2	$\frac{10}{3} P_{20}$	$\frac{2\sqrt{5}}{3} P_{21}$	$\frac{\sqrt{10}}{6} P_{22}$	0	0	0
3/2	$\frac{2\sqrt{5}}{3} P_{21}$	$-\frac{2}{3} P_{20}$	$\frac{2\sqrt{2}}{3} P_{21}$	$\frac{1}{\sqrt{2}} P_{22}$	0	0
1/2	$\frac{\sqrt{10}}{6} P_{22}$	$\frac{2\sqrt{2}}{3} P_{21}$	$-\frac{8}{3} P_{20}$	0	$\frac{1}{\sqrt{2}} P_{22}$	0
-1/2	0	$\frac{1}{\sqrt{2}} P_{22}$	0	$-\frac{8}{3} P_{20}$	$-\frac{2\sqrt{2}}{3} P_{21}$	$\frac{\sqrt{10}}{6} P_{22}$
-3/2	0	0	$\frac{1}{\sqrt{2}} P_{22}$	$-\frac{2\sqrt{2}}{3} P_{21}$	$-\frac{2}{3} P_{20}$	$-\frac{2\sqrt{5}}{3} P_{21}$
-5/2	0	0	0	$\frac{\sqrt{10}}{6} P_{22}$	$-\frac{2\sqrt{5}}{3} P_{21}$	$\frac{10}{3} P_{20}$

Table I. Matrix of  $T_0^{(2)} = S_r^2 - X/3$ . The  $P_{\ell m}$  are associated Legendre polynomials (see Table VI).

M	5/2	3/2	1/2	- 1/2	- 3/2	- 5/2
5/2	$\frac{10}{3} Q_{20}$	$\frac{2\sqrt{5}}{3} Q_{21}^+$	$\frac{\sqrt{10}}{6} Q_{22}^+$	0	0	0
3/2	$\frac{2\sqrt{5}}{3} Q_{21}^-$	$-\frac{2}{3} Q_{20}$	$\frac{2\sqrt{2}}{3} Q_{21}^+$	$\frac{1}{\sqrt{2}} Q_{22}^+$	0	0
1/2	$\frac{\sqrt{10}}{6} Q_{22}^-$	$\frac{2\sqrt{2}}{3} Q_{21}^-$	$-\frac{8}{3} Q_{20}$	0	$\frac{1}{\sqrt{2}} Q_{22}^+$	0
-1/2	0	$\frac{1}{\sqrt{2}} Q_{22}^-$	0	$-\frac{8}{3} Q_{20}$	$-\frac{2\sqrt{2}}{3} Q_{21}^+$	$\frac{\sqrt{10}}{6} Q_{22}^+$
-3/2	0	0	$\frac{1}{\sqrt{2}} Q_{22}^-$	$-\frac{2\sqrt{2}}{3} Q_{21}^-$	$-\frac{2}{3} Q_{20}$	$-\frac{2\sqrt{5}}{3} Q_{21}^+$
-5/2	0	0	0	$\frac{\sqrt{10}}{6} Q_{22}^-$	$-\frac{2\sqrt{5}}{3} Q_{21}^-$	$\frac{10}{3} Q_{20}$

Table II. Matrix of  $T_2^{(2)} = S_+^2/\sqrt{6}$ .  $\langle M | T_{-2}^{(2)} | M' \rangle = \langle M' | T_2^{(2)} | M \rangle^*$ .

$$Q_{20} = \frac{\sqrt{6}}{4} \sin^2 \beta e^{2i\alpha}; \quad Q_{21}^\pm = \sqrt{\frac{3}{2}} \sin \beta (\cos \beta \pm 1) e^{2i\alpha};$$

$$Q_{22}^\pm = \sqrt{\frac{3}{2}} (\cos \beta \pm 1)^2 e^{2i\alpha}.$$

M	5/2	3/2	1/2	-1/2	-3/2	-5/2
5/2	$\frac{15}{2} P_{40}$	$\frac{3\sqrt{5}}{2} P_{41}$	$\frac{3}{8} \sqrt{10} P_{42}$	$\frac{\sqrt{10}}{8} P_{43}$	$\frac{\sqrt{5}}{16} P_{44}$	0
3/2	$\frac{3\sqrt{5}}{2} P_{41}$	$\frac{-45}{2} P_{40}$	$\frac{-15}{\sqrt{8}} P_{41}$	$\frac{-5}{8} \sqrt{2} P_{42}$	0	$\frac{\sqrt{5}}{16} P_{44}$
1/2	$\frac{3}{8} \sqrt{10} P_{42}$	$\frac{-15}{\sqrt{8}} P_{41}$	$15 P_{40}$	0	$\frac{-5}{8} \sqrt{2} P_{42}$	$\frac{-\sqrt{10}}{8} P_{43}$
-1/2	$\frac{\sqrt{10}}{8} P_{43}$	$\frac{-5}{8} \sqrt{2} P_{42}$	0	$15 P_{40}$	$\frac{15}{\sqrt{8}} P_{41}$	$\frac{3}{8} \sqrt{10} P_{42}$
-3/2	$\frac{\sqrt{5}}{16} P_{44}$	0	$\frac{-5}{8} \sqrt{2} P_{42}$	$\frac{15}{\sqrt{8}} P_{41}$	$\frac{-45}{2} P_{40}$	$\frac{-3\sqrt{5}}{2} P_{41}$
-5/2	0	$\frac{\sqrt{5}}{16} P_{44}$	$\frac{-\sqrt{10}}{8} P_{43}$	$\frac{3}{8} \sqrt{10} P_{42}$	$\frac{-3\sqrt{5}}{2} P_{41}$	$\frac{15}{2} P_{40}$

Table III Matrix of  $T_0^{(4)} = \frac{1}{8} [35S_r^4 - 30XS_r^2 + 25S_r^2 - 6X + 3X^2]$ . The  $P_{lm}$  are associated Legendre polynomials (see Table VI).

M	5/2	3/2	1/2	- 1/2	- 3/2	- 5/2
5/2	$\frac{15}{2} R_{40}$	$\frac{3\sqrt{5}}{2} R_{41}^+$	$\frac{3}{8} \sqrt{10} R_{42}^+$	$\frac{\sqrt{10}}{8} R_{43}^+$	$\frac{\sqrt{5}}{16} R_{44}^+$	0
3/2	$\frac{3\sqrt{5}}{2} R_{41}^-$	$-\frac{45}{2} R_{40}$	$-\frac{15}{\sqrt{8}} R_{41}^+$	$-\frac{5}{8} \sqrt{2} R_{42}^+$	0	$\frac{\sqrt{5}}{16} R_{44}^+$
1/2	$\frac{3}{8} \sqrt{10} R_{42}^-$	$-\frac{15}{\sqrt{8}} R_{41}^-$	$15 R_{40}$	0	$-\frac{5}{8} \sqrt{2} R_{42}^+$	$-\frac{\sqrt{10}}{8} R_{43}^+$
-1/2	$\frac{\sqrt{10}}{8} R_{43}^-$	$-\frac{5}{8} \sqrt{2} R_{42}^-$	0	$15 R_{40}$	$\frac{15}{\sqrt{8}} R_{41}^+$	$\frac{3}{8} \sqrt{10} R_{42}^+$
-3/2	$\frac{\sqrt{5}}{16} R_{44}^-$	0	$-\frac{5}{8} \sqrt{2} R_{42}^-$	$\frac{15}{\sqrt{8}} R_{41}^-$	$-\frac{45}{2} R_{40}$	$-\frac{3\sqrt{5}}{2} R_{41}^+$
-5/2	0	$\frac{\sqrt{5}}{16} R_{44}^-$	$-\frac{\sqrt{10}}{8} R_{43}^-$	$\frac{3}{8} \sqrt{10} R_{42}^-$	$-\frac{3\sqrt{5}}{2} R_{41}^-$	$\frac{15}{2} R_{40}$

Table IV. Matrix of  $T_2^{(4)} = -\frac{\sqrt{10}}{8} S_+^2 (X - 9 - 14S_r - 7S_r^2)$ .

$$\langle M | T_{-2}^{(4)} | M' \rangle = \langle M' | T_2^{(4)} | M \rangle^* \quad R_{40} = \frac{\sqrt{10}}{8} s^2 (7c^2 - 1) e^{2i\alpha};$$

$$R_{41}^\pm = \frac{-\sqrt{10}}{4} s(c \pm 1)(1 \pm 7c - 14c^2) e^{2i\alpha}; \quad R_{42}^\pm = 3\sqrt{\frac{5}{2}} (c \pm 1)^2 (1 \mp 7c + 7c^2) e^{2i\alpha};$$

$$R_{43}^\pm = -21\sqrt{\frac{5}{2}} s(c \pm 1)^2 (2c \mp 1) e^{2i\alpha}; \quad R_{44}^\pm = -21\sqrt{10} s^2 (c \pm 1)^2 e^{2i\alpha};$$

M	5/2	3/2	1/2	- 1/2	- 3/2	- 5/2
5/2	$\frac{15}{2} S_{40}^-$	$\frac{3}{2} \sqrt{5} S_{41}^+$	$\frac{3}{8} \sqrt{10} S_{42}^+$	$\frac{\sqrt{10}}{8} S_{43}^+$	$\frac{\sqrt{5}}{16} S_{44}^+$	0
3/2	$\frac{3\sqrt{5}}{2} S_{41}^-$	$-\frac{45}{2} S_{40}$	$-\frac{15}{\sqrt{8}} S_{41}^+$	$-\frac{5}{8} \sqrt{2} S_{42}^+$	0	$\frac{\sqrt{5}}{16} S_{44}^+$
1/2	$\frac{3}{8} \sqrt{10} S_{42}^-$	$-\frac{15}{\sqrt{8}} S_{41}^-$	$15 S_{40}$	0	$-\frac{5}{8} \sqrt{2} S_{42}^+$	$-\frac{\sqrt{10}}{8} S_{43}^+$
-1/2	$\frac{\sqrt{10}}{8} S_{43}^-$	$-\frac{5}{8} \sqrt{2} S_{42}^-$	0	$15 S_{40}$	$\frac{15}{\sqrt{8}} S_{41}^+$	$\frac{3}{8} \sqrt{10} S_{42}^+$
-3/2	$\frac{\sqrt{5}}{16} S_{44}^-$	0	$-\frac{5}{8} \sqrt{2} S_{42}^-$	$\frac{15}{\sqrt{8}} S_{41}^-$	$-\frac{45}{2} S_{40}$	$-\frac{3\sqrt{5}}{2} S_{41}^+$
-5/2	0	$\frac{\sqrt{5}}{16} S_{44}^-$	$-\frac{\sqrt{10}}{8} S_{43}^-$	$\frac{3}{8} \sqrt{10} S_{42}^-$	$-\frac{3\sqrt{5}}{2} S_{41}^-$	$\frac{15}{2} S_{40}$

Table V. Matrix of  $T_{-4}^{(4)} = \frac{\sqrt{70}}{16} S_{+4}'$ .  $\langle M | T_{-4}^{(4)} | M' \rangle = \langle M' | T_4^{(4)} | M \rangle^*$ .

$$S_{40} = \frac{\sqrt{70}}{16} s^4 e^{4i\alpha}; \quad S_{41}^{\pm} = \frac{\sqrt{70}}{4} s^3 (c \pm 1) e^{4i\alpha}; \quad S_{42}^{\pm} = \frac{3}{4} \sqrt{70} s^2 (c \pm 1)^2 e^{4i\alpha};$$

$$S_{43}^{\pm} = \frac{3}{2} \sqrt{70} s (c \pm 1)^3 e^{4i\alpha}; \quad S_{44}^{\pm} = \frac{3}{2} \sqrt{70} (c \pm 1)^4 e^{4i\alpha};$$

$$s = \sin \beta; \quad c = \cos \beta.$$

$\begin{array}{c} l \\ \diagdown \\ m \end{array}$	0	1	2	3	4
0	1				
1	c	-s			
2	$\frac{1}{2}(3c^2 - 1)$	-3sc	$3s^2$		
3	$\frac{1}{2}c(5c^2 - 3)$	$-\frac{3}{2}s(5c^2 - 1)$	$15s^2c$	$-15s^3$	
4	$\frac{1}{8}(35c^4 - 30c^2 + 3)$	$-\frac{5}{2}sc(7c^2 - 3)$	$\frac{15}{2}s^2(7c^2 - 1)$	$-105s^3c$	$105s^4$

Table VI. Associated Legendre Polynomials,  $P_{lm}$ .

(s = sin  $\beta$ , c = cos  $\beta$ )



$$H_1 = H_0 + \Delta_2 - \frac{2V_{53}}{H_1 - \Delta_2} + \frac{V_{31}}{H_1 - \Delta_1} - \frac{V_{51}}{2H_1 - \Delta_{12}} + \frac{V_{3,-1}}{2H_1 - \Delta_1} - \frac{V_{5,-1}}{3H_1 - \Delta_{12}} - \frac{2\Delta_2 V_{5,-3}}{16H_1^2 - \Delta_2^2}$$

$$H_2 = H_0 + \Delta_1 + \frac{V_{53}}{H_2 - \Delta_2} - \frac{2V_{31}}{H_2 - \Delta_1} - \frac{V_{51}}{2H_2 - \Delta_{12}} - \frac{2\Delta_1 V_{3,-1}}{4H_2^2 - \Delta_1^2} + \frac{V_{5,-1}}{3H_2 + \Delta_{12}} - \frac{V_{5,-3}}{4H_2 + \Delta_2}$$

$$H_3 = H_0 + \frac{2H_3 V_{31}}{H_3^2 - \Delta_1^2} + \frac{4H_3 V_{51}}{4H_3^2 - \Delta_{12}^2} - \frac{4H_3 V_{3,-1}}{4H_3^2 - \Delta_1^2} - \frac{6H_3 V_{5,-1}}{9H_3^2 - \Delta_{12}^2}$$

$$H_4 = H_0 - \Delta_1 + \frac{V_{53}}{H_4 + \Delta_2} - \frac{2V_{31}}{H_4 + \Delta_1} - \frac{V_{51}}{2H_4 + \Delta_{12}} + \frac{2\Delta_1 V_{3,-1}}{4H_4^2 - \Delta_1^2} + \frac{V_{5,-1}}{3H_4 - \Delta_{12}} - \frac{V_{5,-2}}{4H_4 - \Delta_2}$$

$$H_5 = H_0 - \Delta_2 - \frac{2V_{53}}{H_5 + \Delta_2} + \frac{V_{31}}{H_5 + \Delta_1} - \frac{V_{51}}{2H_5 + \Delta_{12}} + \frac{V_{3,-1}}{2H_5 + \Delta_1} - \frac{V_{5,-1}}{3H_5 + \Delta_{12}} + \frac{2\Delta_2 V_{5,-3}}{16H_5^2 - \Delta_2^2}$$

Table VII. Line Position Formulas.  $H_0 = \hbar\omega/g\beta_0$ ,  $H_1$  corresponds to the  $(E_{5/2} - E_{3/2})$  transition, etc.

$$g\beta_o\Delta_1 = (1 - 3c^2) C_{20} - \sqrt{6} s^2 c_{22} C_{22} + \frac{75}{16} (3 - 30c^2 + 35c^4) C_{40} \\ + \frac{75}{16} \sqrt{70} s^4 c_{44} C_{44} - \frac{75}{8} \sqrt{10} s^2 (1 - 7c^2) c_{42} C_{42}$$

$$g\beta_o\Delta_2 = 2(1 - 3c^2) C_{20} - 2\sqrt{6} s^2 c_{22} C_{22} - \frac{15}{4} (3 - 30c^2 + 35c^4) C_{40} \\ - \frac{15}{4} \sqrt{70} s^4 c_{44} C_{44} + \frac{15}{2} \sqrt{10} s^2 (1 - 7c^2) c_{42} C_{42}$$

$$g^2\beta_o^2 V_{5,3} = 20s^2 \left[ \frac{2}{\sqrt{6}} s_{22} C_{22} - \frac{3}{8} \sqrt{10} (1 - 7c^2) s_{42} C_{42} + \frac{3}{8} \sqrt{70} s^2 s_{44} C_{44} \right]^2 \\ + 20s^2 c^2 \left[ C_{20} - \frac{2}{\sqrt{6}} c_{22} C_{22} - \frac{15}{8} (3 - 7c^2) C_{40} \right. \\ \left. + \frac{3}{4} \sqrt{10} (4 - 7c^2) c_{42} C_{42} - \frac{3}{8} \sqrt{70} s^2 c_{44} C_{44} \right]^2$$

$$g^2\beta_o^2 V_{3,1} = 8s^2 \left[ \frac{2}{\sqrt{6}} s_{22} C_{22} + \frac{15}{16} \sqrt{10} (1 - 7c^2) s_{42} C_{42} - \frac{15}{16} \sqrt{70} s^2 s_{44} C_{44} \right]^2 \\ + 8s^2 c^2 \left[ C_{20} - \frac{2}{\sqrt{6}} c_{22} C_{22} + \frac{75}{16} (3 - 7c^2) C_{40} \right. \\ \left. - \frac{15}{8} \sqrt{10} (4 - 7c^2) c_{42} C_{42} + \frac{15}{16} \sqrt{70} s^2 c_{44} C_{44} \right]^2$$

$$g^2\beta_o^2 V_{5,1} = \frac{5}{2} \left[ s^2 C_{20} + \frac{2}{\sqrt{6}} (1 + c^2) c_{22} C_{22} - \frac{45}{8} s^2 (1 - 7c^2) C_{40} \right. \\ \left. + \frac{9}{4} \sqrt{10} (1 - 6c^2 + 7c^4) c_{42} C_{42} + \frac{9}{8} \sqrt{70} s^2 (1 + c^2) c_{44} C_{44} \right]^2 \\ + 10 c^2 \left[ \frac{2}{\sqrt{6}} s_{22} C_{22} - \frac{9}{8} \sqrt{10} (5 - 7c^2) s_{42} C_{42} + \frac{9}{8} \sqrt{70} s^2 s_{44} C_{44} \right]^2$$

Table VIII. Formulas supplementary to Table VII. (Continued on next page)

$$\begin{aligned}
g^2 \beta_o^2 V_{3, -1} &= \frac{9}{2} \left[ s^2 C_{20} + \frac{2}{\sqrt{6}} (1 + c^2) c_{22} C_{22} + \frac{25}{8} s^2 (1 - 7c^2) C_{40} \right. \\
&\quad \left. - \frac{5}{4} \sqrt{10} (1 - 6c^2 + 7c^4) c_{42} C_{42} - \frac{5}{8} \sqrt{70} s^2 (1 + c^2) c_{44} C_{44} \right]^2 \\
&\quad + 18c^2 \left[ \frac{2}{\sqrt{6}} s_{22} C_{22} + \frac{5}{8} \sqrt{10} (5 - 7c^2) s_{42} C_{42} - \frac{5}{8} \sqrt{70} s^2 s_{44} C_{44} \right]^2 \\
g^2 \beta_o^2 V_{5, -1} &= \frac{3^2 \cdot 5^2 \cdot 7}{4} s^2 \left\{ c^2 \left[ \frac{\sqrt{70}}{2} s^2 C_{40} + 2\sqrt{7} c^2 c_{42} C_{42} \right. \right. \\
&\quad \left. \left. - (3 + c^2) c_{44} C_{44} \right]^2 + \left[ \sqrt{7} (1 - 3c^2) s_{42} C_{42} + (1 + 3c^2) s_{44} C_{44} \right]^2 \right\} \\
g^2 \beta_o^2 V_{5, -3} &= \frac{3^2 \cdot 5^2 \cdot 7}{8} \left[ \sqrt{70} s^4 C_{40} - 4\sqrt{7} s^2 (1 + c^2) c_{42} C_{42} \right. \\
&\quad \left. + 2(1 + 6c^2 + c^4) c_{44} C_{44} \right]^2 \\
&\quad + \frac{3^2 \cdot 5^2 \cdot 7c^2}{8} \left[ \sqrt{7} s^2 s_{42} C_{42} - (1 + c^2) s_{44} C_{44} \right]^2
\end{aligned}$$

$$\Delta_{12} \equiv \Delta_1 + \Delta_2$$

$$s = \sin \beta$$

$$c = \cos \beta$$

$$s_{22} = \sin 2(\alpha - \lambda_{22})$$

$$c_{22} = \cos 2(\alpha - \lambda_{22})$$

$$s_{44} = \sin 4(\alpha - \lambda_{44})$$

$$c_{44} = \cos 4(\alpha - \lambda_{44})$$

$$s_{42} = \sin 2(\alpha - \lambda_{42})$$

$$c_{42} = \cos 2(\alpha - \lambda_{42})$$

Table VIII. Formulas supplementary to Table VII.

M	5/2	1/2	- 3/2	- 5/2	- 1/2	3/2
5/2	$\frac{5}{2}G + \frac{10}{3}C_{20}$ $+ \frac{15}{2}C_{40}$	$2\sqrt{\frac{5}{3}}C_{22}e^{-2i\lambda}$ $+ \frac{45}{2}C_{42}e^{-2i\lambda}$	$\frac{15}{2}\sqrt{14}C_{44}e^{-4i\lambda}$			
1/2	$2\sqrt{\frac{5}{3}}C_{22}e^{2i\lambda}$ $+ \frac{45}{2}C_{42}e^{2i\lambda}$	$\frac{1}{2}G - \frac{8}{3}C_{20}$ $+ 15C_{40}$	$2\sqrt{3}C_{22}e^{-2i\lambda}$ $- \frac{15}{2}\sqrt{5}C_{42}e^{-2i\lambda}$			
-3/2	$\frac{15}{2}\sqrt{14}C_{44}e^{4i\lambda}$	$-\frac{15}{2}\sqrt{5}C_{42}e^{2i\lambda}$ $+ 2\sqrt{3}C_{22}e^{2i\lambda}$	$-\frac{3}{2}G - \frac{2}{3}C_{20}$ $- \frac{45}{2}C_{40}$			
-5/2				$-\frac{5}{2}G + \frac{10}{3}C_{20}$ $+ \frac{15}{2}C_{40}$	$2\sqrt{\frac{5}{3}}C_{22}e^{2i\lambda}$ $+ \frac{45}{2}C_{42}e^{-2i\lambda}$	$\frac{15}{2}\sqrt{14}C_{44}e^{4i\lambda}$
-1/2				$2\sqrt{\frac{5}{3}}C_{22}e^{-2i\lambda}$ $+ \frac{45}{2}C_{42}e^{-2i\lambda}$	$-\frac{1}{2}G - \frac{8}{3}C_{20}$ $+ 15C_{40}$	$-\frac{15}{2}\sqrt{5}C_{42}e^{2i\lambda}$ $+ 2\sqrt{3}C_{22}e^{2i\lambda}$
3/2					$-\frac{15}{2}\sqrt{5}C_{42}e^{-2i\lambda}$ $+ 2\sqrt{3}C_{22}e^{-2i\lambda}$	$\frac{3}{2}G - \frac{2}{3}C_{20}$ $- \frac{45}{2}C_{40}$

Table IX. Spin-Hamiltonian matrix for  $C_2$  symmetry,  
for  $\underline{H}$  parallel to the two-fold axis.  $G \equiv g\beta_0 H$ .

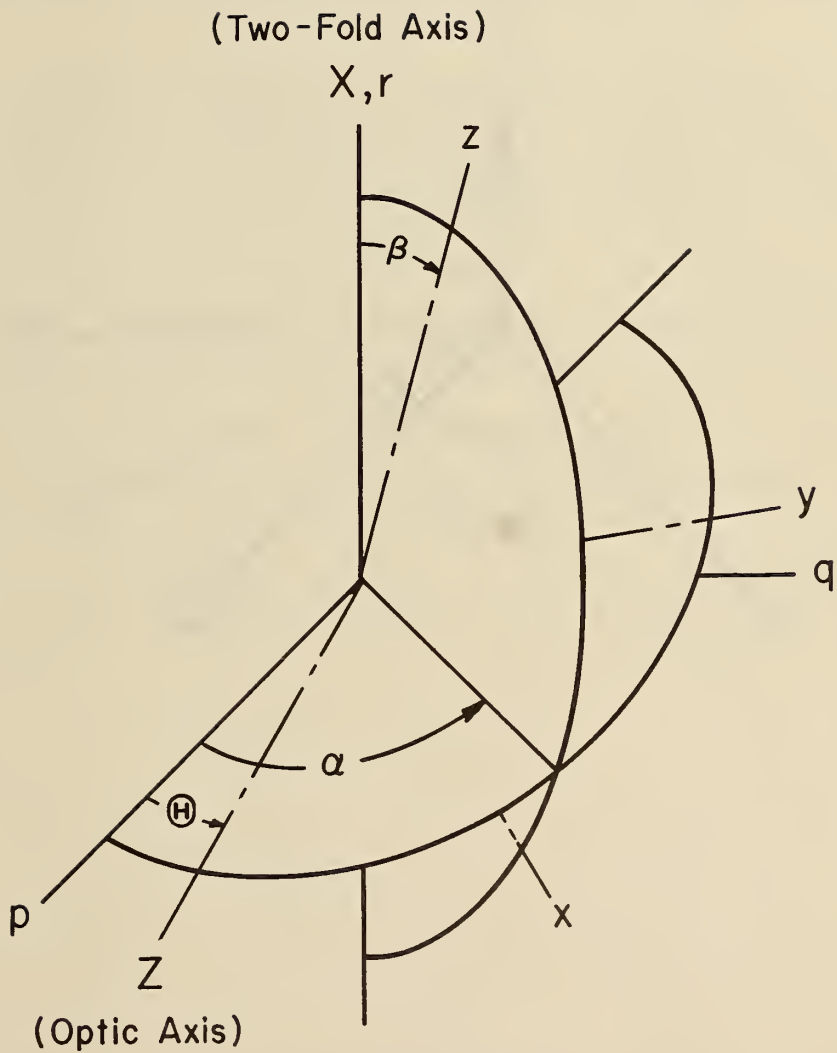


Figure 1. Relation between the p, q, r crystalline electric field axes and the x, y, z quantization axes. The optic axis (Z) of the quartz crystal is also shown.

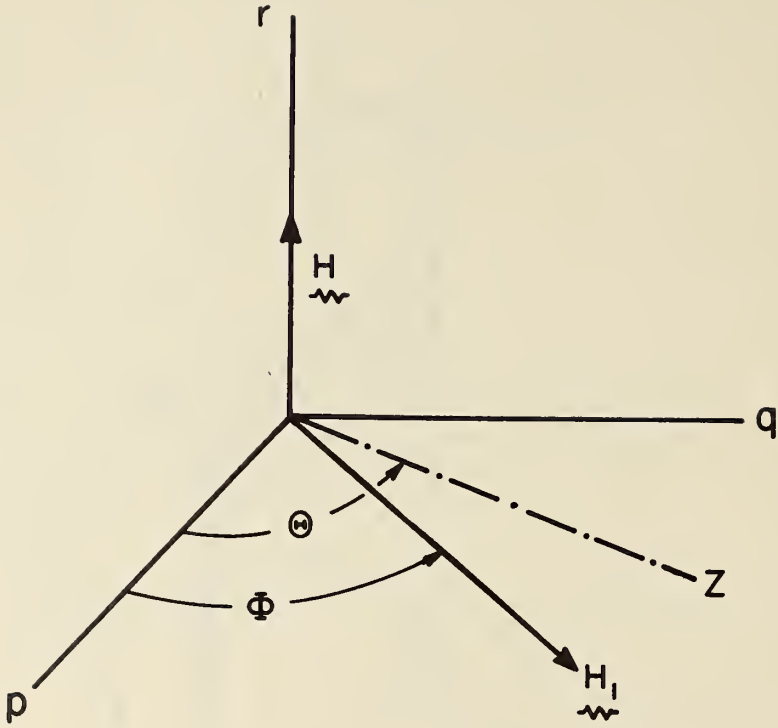


Figure 2. The orientation of the microwave field  $H_1$  in the  $p, q$  plane, used in the line-intensity analysis. The optic axis ( $Z$ ) is also shown.



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